Short- and long-chain perfluoroalkyl substances in the water, suspended particulate matter, and surface sediment of a turbid river

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HIGHLIGHTS

- Short-chain PFASs could reach up to 88.8% of the total PFAS concentration in water.
- Long-chain PFASs prevailed in the sediment and SPM.
- $\log K_d$ of PFASs between sediment/SPM and water was positively correlated with $\log K_{ow}$.
- PFAS concentration in SPM was negatively correlated with SPM concentration in water.
- The total annual river flux of the eleven studied PFASs was estimated at 3.88 tons.

GRAPHICAL ABSTRACT
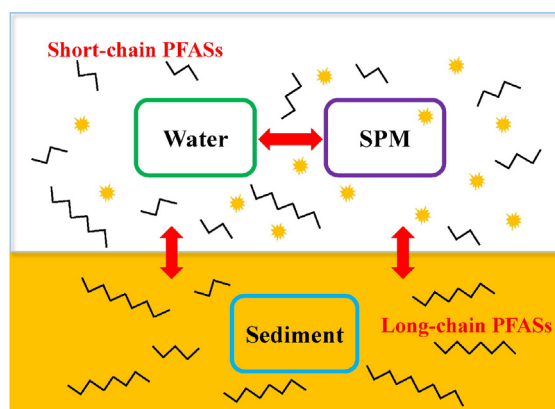
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ABSTRACT

Perfluoroalkyl substances (PFASs) have attracted attentions all around the world. However, little is known about their distribution among water, suspended particulate matter (SPM), and sediment phases in rivers, especially for the short-chain PFASs. In this work, the Yellow River, the largest turbid river in the world, was selected as a case to study eleven kinds of PFASs in the three phases of rivers. These PFASs included C4–C12 perfluorinated carboxylates (PFCAs), perfluorobutyl sulfonate (PFBS), and perfluorooctansulfonate (PFOS), among which C4–C7 PFCAs and PFBS belong to short-chain PFASs, while C8–C12 PFCAs and PFOS belong to long-chain PFASs. The results showed that the total PFAS concentration ranged from 44.7 ng L^{-1} to 1.52 μg L^{-1} in the water, from 8.19 to 17.4 ng g^{-1} in the sediment, and from 3.44 to 14.7 ng g^{-1} in the SPM. Short-chain PFASs predominated in the water and could reach up to 88.8% of the total PFAS concentration in water, while long-chain PFASs prevailed in the sediment and SPM. The PFAS concentration in SPM showed a significant negative correlation with SPM concentration in river water ($p < 0.01$). The distribution coefficients (K_d) of PFASs between sediment/SPM and water increased with their chain length and there was a positive correlation between $\log K_d$ and $\log K_{ow}$ (octanol-water partition coefficients). The total annual flux of all the eleven PFASs was estimated at 3.88 tons for the Yellow River into the Bohai Sea, among which the PFOA flux was the highest (0.90 tons). The widely

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occurrence and high concentrations of short-chain PFASs in the Yellow River indicates the shift of manufacturing focus of perfluoroalkyl chemicals from traditional long-chain ones to short-chain ones. Further studies should be conducted to evaluate the eco-environmental risks of these short-chain PFASs in water environments.

1. Introduction

Perfluoroalkyl substances (PFASs) are organofluorine compounds in which all of the hydrogen atoms on the carbon chain are replaced by fluorine atoms (Buck et al., 2011). C—F bond is the strongest covalent bond due to the strong electron drawing effect of fluorine (O'Hagan, 2008), which results in the thermally inertness of PFASs. The enduring properties and their hydrophobic/lipophobic nature make PFASs highly useful in industrial and commercial applications. Since 1950s, PFASs have been widely used as protectants for textiles, stain repellents, personal care products, pesticides, fire-fighting forms, emulsifying agents, etc. (Zushi et al., 2012).

PFASs have been detected all around the world, even in the snow from polar regions of Earth (Young et al., 2007). The concentrations of many kinds of PFASs in multiple media have been reported in recent years, including tap water (Mak et al., 2009; Schwanz et al., 2016), groundwater (Loos et al., 2010), surface water (Ju et al., 2008; Zhao et al., 2014; Lorenzo et al., 2016; Sharma et al., 2016), snow fall and biota (Yeung et al., 2009; Butt et al., 2010). Many studies found that perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) were the dominant compounds and they were believed to be the final transformation products of other PFASs (Dinglasan et al., 2004; Parsons et al., 2008; Zhao et al., 2014).

Many investigators have found that PFASs could be accumulated by aquatic organisms (Conder et al., 2008; Xia et al., 2013). Previous studies have demonstrated that some PFASs may induce toxic effects on test organisms. For example, PFOA and PFOS may have reproductive and developmental toxicity on rodents (Lau et al., 2004); PFOA may exert hepatic toxic and have potential carcinogenicity on rats (Kennedy et al., 2004). Thus PFASs may have adverse effects on wild life and even human beings through the food web (Kannan et al., 2005). Therefore, PFOS and its salts have been added to Annex B of the Stockholm Convention on Persistent Organic Pollutants in May, 2009. The use and production of PFOS were restricted in the ratifying countries (179 parties in 2014, including China). In 2002, 3M company, the principal manufacturer (estimated 80–90% market share), phased out the production of POSF-based (perfluorooctyl sulfonyl fluoride) products (Weppner, 2000). After that, some "old" PFASs were replaced by "new" ones which have shorter chain length. For example, PFOS was replaced by perfluorobutane sulfonate (PFBS) by 3M Company after 2003. It has been reported that short-chain PFASs are as persistent as and more mobile in long-range transport than the long-chain homologues (Wang et al., 2015). After many years of replacing traditional PFASs, whether these substitutes have reached the same level as the old ones and they have the same environmental fate like their predecessors should be well studied.

The properties and fate of PFASs are closely related to their chain length (C_nF_{2n+1}). Short-chain PFASs, which are defined as $n < 6$ for perfluorosulfonic acids (PFSAs) and $n < 7$ for perfluorocarboxylic acids (PFCAs) (OECD, 2011), have been detected and even prevail over long-chain PFASs in some places. For example, short-chain PFASs (C4–C6) were detected with a comparable level of the longer-chain PFASs (>C6) in the water samples from Dagu Drainage Canal (Dagu) in Tianjin, China, and perfluorobutyric acid (PFBA) was the dominant type in the short-chain analogues (Yao et al., 2014). Perfluoropentanoate (PFPnA), perfluoroheptanoate (PFHpA), and PFOA were the dominant PFASs in the Northwest Pacific Ocean and PFPnA dominated in the Bering Sea (Cai et al., 2012). However, most previous studies focused on the short-chain PFASs in water, little research is about their occurrence in suspended particulate matters (SPM) and sediments in aquatic

environment. Hydrophobic organic compounds (HOCs) tend to be associated with sediment and SPM, which play important roles in controlling the fate and bioavailability of HOCs in aquatic environment, especially in turbid rivers (Ahrens et al., 2010; Dong et al., 2013). Because the fluorocarbon chains of PFASs are both hydrophobic and lipophobic, their distribution may be different from other well studied HOCs in rivers. However, little is known about the distribution of short-chain PFASs among water, SPM, and sediment.

Because the Yellow River is the largest turbid river in the world (Liu et al., 2013), this study took it as a typical case to investigate the PFAS distribution in turbid rivers, for both short-chain and long-chain ones. The studied short-chain PFASs included C4–C7 PFCAs and PFBS, and long-chain PFASs included C8–C12 PFCAs and PFOS. The main objective of this research was to study the occurrence of short-chain & long-chain PFASs along the middle and lower reaches of the Yellow River, which is subject to intensive anthropogenic influences. The distribution behaviors between sediment and water, as well as between SPM and water were examined, and the annual flux of PFASs into the Bohai Sea was estimated.

2. Materials and methods

2.1. Chemicals and reagents

PFOS (98%) and PFOA (96%) were purchased from AccuStandard Inc. (New Haven, USA). PFBA (99%) and perfluoroundecanoic acid (PFUdA, 96%) were obtained from Matrix Scientific Trade Co. (Columbia, USA). PFPnA (98%), PFHpA (98%), and perfluorononanoic acid (PFNA, 97%) were supplied by Tokyo Chemical Industries (Tokyo, Japan). PFBS (98%), perfluorohexanoic acid (PFHxA, 98%), perfluorodecanoic acid (PFDA, 98%), and perfluorododecanoic acid (PFDoA, 95%) were purchased from Acros Organics (New Jersey, USA). The physicochemical parameters of the studied PFASs are listed in Table S1. The stock solution of these PFASs was prepared with 80:20 (v:v) methanol/water at a concentration of 200 mg L^{-1} for each kind of PFAS. Chromatography grade methanol was purchased from J.T. Baker of Phillipsburg (NJ, USA). [1,2,3,4-$^{13}C_4$] perfluorooctanoic acid (mass labelled PFOA, MPFOA) (≥99%), used as recovery indicator, was supplied by Wellington Laboratories (Guelph, Canada). Ammonium acetate (98%) and tetrabutylammonium hydrogen sulfate (TBA, 99%) were obtained from Amethyst Chemicals of J&K Scientific Ltd. (Beijing, China). Methyl-tert-butyl ether (MTBE, 99.5%) was purchased from Acros Organics (New Jersey, USA). Any water used in this study was produced by a MilliQ purification system (Millipore, Germany).

2.2. Sample collection

Water and sediment samples were collected from 20 sites along the middle and lower reaches of the Yellow River, 14 of which were at the main stream and the other 6 sites were at major tributaries (Fig. 1, detailed information can be seen in Table S2). The sampling process lasted from Aug. 31st to Sept. 26th of 2013, which was in the normal flow period of the Yellow River. At each sampling site, three surface sediment samples (0–10 cm) were collected with a shovel within 1 m^2 area; each sub-sample was about 200 g and they were stored in polyethylene (PE) valve bags, respectively. The samples at each sampling site were mixed thoroughly after they were transported to laboratory. Water samples were collected with a pre-rinsed metal pail from river and pre-treated on site. Specifically, each water sample was filtered through a pre-weighted glass fiber membrane (GF/F, Whatman®, 0.7 μm) to